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Pairwise-Substitution Effects and Intramolecular Hydrogen Bonds in Nitrophenols and Methylnitrophenols. Thermochemical Measurements and ab Initio Calculations

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The standard molar enthalpies of formation in the gaseous state of a series of nitrophenols, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 5-methyl-2-nitrophenol, 2-methyl-5-nitrophenol, and 3-methyl-4-nitrophenol, have been obtained from combustion calorimetry and results from the temperature dependence of the vapor pressure measured by the transpiration method. To verify the experimental data, ab initio calculations of all compounds have been performed using MP, DFT, and G3 methods. Enthalpies of formation derived from the G3 methods are in a good agreement with the experimental results. The quantitative analysis of ortho, meta, and para pairwise-substituent effects in nitrophenols has been performed, and the strength of intramolecular hydrogen bonding in *o*-nitrophenol has been derived from thermochemical results and compared with those obtained from spectroscopic experiments and ab initio calculations. The new results help to resolve uncertainties in the available thermochemical data on extended series of nitrophenols.

Introduction

Hydrogen bonding determines the spatial structure of many molecules and also plays an important role in processes such as selective binding and molecular recognition. Although ortho-substituted benzenes are probably the most commonly cited examples of intramolecular hydrogen bonding, there are still not enough thermodynamic data available to enable the formulation of a general rule regarding the quantitative values for its strength.[1−2] We have commenced studies on the thermochemical properties of ortho-substituted benzenes[3] with the aim to enlarge insight into the energetic situation of intramolecular hydrogen bonds (HB).

It is well-established that *o*-nitrophenol exists as mixtures of two isomers, a trans form with the hydroxyl hydrogen pointed away from the nitro group and a cis form, which is stabilized by hydrogen bonding. The presence of these two isomers is evidenced by two bands in the O−H stretching region of the infrared spectrum for *o*-nitrophenol both in solution and in the vapor phase.[4] The strength of the HB has also been extensively investigated using IR spectroscopy[5,6] and chromatograpy[7] with a considerable spread of values within (25−35 kJ·mol^{-1}). Modern ab initio calculations (DFT methods)[2,8] define the strength of the HB as the energy difference between the cis and trans isomers of *o*-nitrophenol, which is predicted on the somewhat higher level of 45−50 kJ·mol^{-1}. In this work, we suggest an alternative way to derive HB strength from thermochemical measurements of gaseous enthalpies of formation, $\Delta_f H^\circ_m$(g), of a series of nitrophenols and methylnitrophenols (or nitrocresols) presented in Figure 1. Considering that the enthalpy of formation, $\Delta_f H^\circ_m$(g), implies an inherent energetic characteristics of a molecule, thermochemistry is particularly suited for this purpose. To get quantitative information on the strength of hydrogen bonding, thermochemical measurements (combustion calorimetry and vapor-pressure measurements) have been performed for ortho-, meta-, and para-substituted nitrophenols and nitrocresols as shown Figure 1. From these data, the enthalpies of formation $\Delta_f H^\circ_m$(g) have been obtained. With the use of these results, the values of the pairwise interactions of substituents (OH, NO_2, and CH_3) on the benzene ring as well as the strength of the HB in *o*-nitrophenol have been derived.

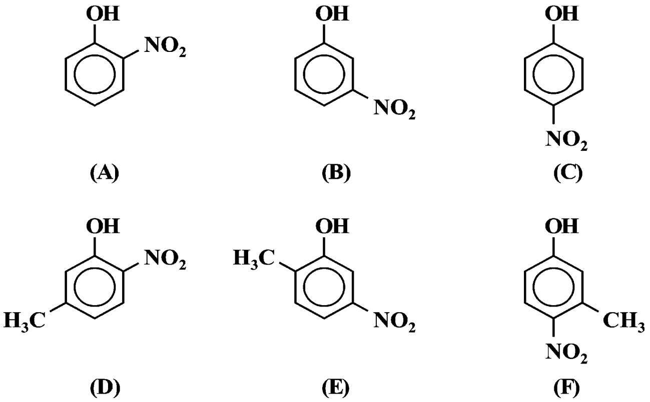

Figure 1. Structures of nitrophenols and nitrocresols (methylnitrophenols) studied in this work: (A), 2-nitrophenol; (B), 3-nitrophenol; (C), 4-nitrophenol; (D), 5-methyl-2-nitrophenol; (E), 2-methyl-5-nitrophenol; (F), 3-methyl-4-nitrophenol.

For the validation of the experimental data on nitrophenols and nitrocresols, high-level ab initio calculations of $\Delta_f H^\circ_m$(g) of these molecules have been performed using the *Gaussian-03* program package. Absolute electronic energy values of the molecules have been obtained using MP, DFT, and G3 methods.

Experimental Section

Materials. Samples of nitrophenols and nitrocresols (purchased from Aldrich) with a mass-fraction purity of about 0.99 were purified by repeated fractional sublimation at reduced pressure and in darkness. Examination of the samples using GC showed no discernible amounts of impurities. The products were analyzed using a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and Hewlett-

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Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 $cm^3 \cdot s^{-1}$. A capillary column HP-5 (stationary phase cross-linked 5% PH ME silicone) of column length 25 m, inside diameter 0.32 mm, and film thickness 0.25 μm was used. The standard temperature program of the GC was $T = 323$ K, followed by a heating rate of 0.167 $K \cdot s^{-1}$ to $T = 523$ K. The fresh sublimed samples of nitrophenols and nitrocresols were subjected to a pellet-drying procedure in order to remove traces of occluded water and were kept in a desiccator under P_2O_5 before starting the combustion experiments. At room temperature, 4-nitrophenol exists as stable yellow crystals, which were used for combustion calorimetry.

Combustion Calorimetry. An isoperibol bomb calorimeter was used to measure the energy of combustion of the nitrophenols and nitrocresols. The detailed procedure has been described previously.[9] The substances were pressed into pellets of mass ≈700 mg and were burned in oxygen at a pressure of 3.04 MPa with a mass of 1.00 g of water added to the bomb. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter, ϵ_{calor}, was determined with a standard reference sample of benzoic acid (sample SRM 39i, N.I.S.T.). From nine experiments, ϵ_{calor} was measured to be 14812.12 ± 0.74 $J \cdot K^{-1}$. Correction for nitric acid formation was based on the titration with 0.1 $mol \cdot dm^{-3}$ NaOH(aq). The atomic weights used were those recommended by the IUPAC Commission.[10] The sample masses were reduced to vacuum using densities of the solid nitrophenols.[11−13] For nitrocresols, the densities ρ(293 K) were measured using a calibrated pycnometer. The energy of combustion of the cotton thread $\Delta_c u°(CH_{1.774}O_{0.887}) = -(16945.2 \pm 4.2)$ $J \cdot g^{-1}$ was measured earlier. For converting the energy of the actual bomb process to that of the isothermal process and reducing to standard conditions, the conventional procedure[14] was applied.

Transpiration Method. Vapor pressures, enthalpies of vaporization, $\Delta_l^g H_m$, and enthalpies of sublimation, $\Delta_{cr}^g H_m$, of nitrophenols were determined by using the method of transference in a saturated stream of nitrogen. The method has been described before[15−16] and has proven to give results in agreement with other established techniques for determining vapor pressures and enthalpies of vaporization of pure substances from the temperature dependence of the vapor pressure. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U tube of length 10 cm and diameter 0.5 cm. A preheated nitrogen stream was passed through the U tube at a constant temperature (±0.1 K). The flow rate of the nitrogen stream was measured using a soap-bubble flow meter (±0.2−0.3%) and optimized to reach the saturation equilibrium of the transporting gas at each temperature under study. We tested our apparatus at different flow rates of the carrier gas to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired contribution. In our apparatus, the contribution due to diffusion was negligible at a flow rate down to 0.5 $dm^3 \cdot h^{-1}$. The upper limit for our apparatus was at a flow rate of 7.5 $dm^3 \cdot h^{-1}$. Thus, we carried out the experiments in the flow-rate interval of 2−3.5 $dm^3 \cdot h^{-1}$, which ensured that the transporting gas was in saturated equilibrium with the coexisting condensed phase in the saturation tube. The amount of material transported was collected in a cold trap at 243 K. The mass of compound collected within a certain time interval was determined by dissolving it in a suitable solvent with a certain amount of external standard (hydrocarbon). This solution was analyzed using a gas chromatograph equipped with an autosampler. The uncertainty of the sample amount determined by GC analysis was assessed to be within 1−3%. The peak area of the compound related to the peak of the external standard (hydrocarbon n-C_nH_{2n+2}) is a direct measure of the mass of the compound condensed into the cooling trap, provided that a calibration run has been made. The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time, and the small value of the residual vapor pressure at the temperature of condensation was added. The latter was calculated from a linear correlation between $\ln(p_i^{sat})$ and T^{-1} obtained by iteration. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated according to

$$p_i^{sat} = m_i R T_a / V M_i; \quad V = V_{N2} + V_i; \quad (V_{N2} \gg V_i) \qquad (1)$$

where $R = 8.314472$ $J \cdot K^{-1} \cdot mol^{-1}$; m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is the volume contribution of the substance i to the gaseous phase. V_{N2} is the volume of transporting gas and T_a is the temperature of the soap-bubble meter. V_{N2} was determined from flow rate and time measurements.

Quantum Chemical Calculations. Ab initio calculations of the nitrobenzene derivatives using DFT methods have long been a popular endeavor.[18−21] The DFT methods require a moderate expense of time and provide good results for normal frequencies of molecules while the electronic energies of the molecules are not always predicted in a satisfying way. G3 methods provide more reliable results concerning electronic energies and are therefore preferably used for calculating thermodynamic quantities such as enthalpies of formation and enthalpies of reaction.[22] In this work, we have applied a number of methods of different sophistication: MP2/6-31G(d,p), MP2/6−3111++G(d,p), two DFT methods of B3LYP/6-31 G(d,p) and DFT B3LYP/6-311+G(d,p), and two methods from the G3 series (G2MP2 and G3MP2) for predicting the gaseous enthalpies of formation of nitrophenols and nitrocresols. Standard ab initio molecular orbital calculations were performed with the *Gaussian 03*, revision 04 series of programs.[23] The enthalpy value of the studied compounds at $T = 298$ K was evaluated according to standard thermodynamic procedures.[24]

Results and Discussion

The enthalpy of formation in the gaseous phase of any compound is made up of two contributions: $\Delta_f H°_m(g) = \Delta_f H°_m(cr) + \Delta_{cr}^g H_m$, where $\Delta_f H°_m(cr)$ is the enthalpy of formation in the crystalline state and $\Delta_{cr}^g H_m$ is the enthalpy of sublimation. Contradictory experimental results are available from the literature for these three thermodynamic properties and are collected in Table 1. While experimental values of $\Delta_f H°_m(cr)$ of 2-nitrophenol[11,13] are in very close agreement, the data[11−13] of $\Delta_f H°_m(cr)$ for 3- and 4-nitrophenol are in substantial disagreement of 5−12 $kJ \cdot mol^{-1}$. The situation is even more troublesome for the data available for $\Delta_{cr}^g H_m$ (see Table 2), where the spread of the available results is unacceptable large at 8−30 $kJ \cdot mol^{-1}$. Thus, to ascertain the thermodynamic properties of nitrophenols, new thermochemical measurements of 2-, 3- and 4-nitrophenols are required. We have reproduced the combustion enthalpy of 2-nitrophenol (where two coinciding values are available) to check our techniques and data treatment (see Table 1). This fact has encouraged further calorimetric investigations. The transpiration method has never been applied before to vapor-pressure measurements of nitrophenols for

TABLE 1: Thermochemical Results on Nitrophenols and Nitrocresols at $T = 298.15$ K in kJ·mol^{-1}

compounds	$\Delta_c H^\circ_m$(cr)	$\Delta_f H^\circ_m$(cr)	$\Delta^g_{cr} H_m^b$	$\Delta_f H^\circ_m(g)^c$	$\Delta_f H^\circ_m(g)^d$
2-nitrophenol	−2871.0 ± 1.3[13]	−204.6 ± 1.4			
	−2873.3 ± 0.6[11]	−202.4 ± 1.0			
	−2874 ± 0.8[a]	−203.2 ± 1.1[a]	75.4 ± 0.4	−127.8 ± 1.2	−125.6
3-nitrophenol	−2875.1 ± 0.9[13]	−200.5 ± 1.0			
	−2863.2 ± 0.5[11]	−212.4 ± 1.0			
	−2870.0 ± 1.5[12]	−205.7 ± 1.7			
	−2868.2 ± 1.0[a]	−209.3 ± 1.3[a]	97.5 ± 0.3	−111.8 ± 1.3	−112.2
4-nitrophenol	−2868.5 ± 1.0[13]	−207.1 ± 1.1			
	−2863.2 ± 0.5[11]	−212.4 ± 1.0			
	−2863.0 ± 0.9[a]	−214.5 ± 1.2[a]	100.4 ± 0.2	−114.1 ± 1.2	−115.9
5-methyl-2-nitrophenol	−3506.6 ± 0.9[a]	−249.0 ± 1.3[a]	81.4 ± 0.3	−167.6 ± 1.3	−162.2
2-methyl-5-nitrophenol	−3505.7 ± 0.6[a]	−249.9 ± 1.1[a]	102.7 ± 0.3	−147.2 ± 1.1	−150.7
3-methyl-4-nitrophenol	−3502.4 ± 0.8[a]	−253.2 ± 1.2[a]	108.3 ± 0.4	−144.9 ± 1.3	−142.5

[a] This work, from combustion experiments (see Table 3). [b] This work, from the measurements of vapor pressure at different temperatures (Tables 2 and 4). [c] Derived from results measured in this work (column 3 and column 4). [d] Calculated in this work using G3MP2 (see text).

TABLE 2: Compilation of Data on Enthalpies of Sublimation, $\Delta^g_{cr}H_m$, of Nitrophenols and Nitrocresols

	technique[a]	temperature range (K)	$\Delta^g_{cr}H_m(T)$ (kJ·mol^{-1})	$\Delta^g_{cr}H_m$(298 K)[b] (kJ·mol^{-1})	ref
2-nitrophenol (cr)	TE	298−310	73.2 ± 1.3	73.4 ± 2.1	28
	K	304−314	85.1	85.5	29
	N/A	273−292		54.4	30
	C	298.15		72.3 ± 0.3	13
	T	281.3−316.2	75.4 ± 0.4	75.4 ± 0.4	this work
2-nitrophenol (l)	E	322−488		59.0[c]	31
	K	324−347	40.7	43.3[c]	29
	N/A	366−490		61.0[c]	30
	T	319.2−346.2	56.0 ± 0.5	58.4 ± 0.5[c]	this work
3-nitrophenol (cr,II)	TE	325−336	91.6 ± 1.7	92.4 ± 2.1	28
	K	305−334		76.8	30
	K	316.2−330.1	98.9 ± 0.6	99.6 ± 0.6	12
	C	333	90.1 ± 0.5	91.0 ± 0.5	13
	T	323.2−355.2	96.5 ± 0.3	97.5 ± 0.3	this work
3-nitrophenol (l)				80.1[c,d]	this work
4-nitrophenol (cr)	TE	339−351	91.2 ± 1.7	92.4 ± 1.7	28
	K	305.1−351.7	98.8 ± 1.0	99.6 ± 1.0	32
	N/A	304−352		99.6	30
	C	333	91.0 ± 0.4	91.9 ± 0.4	13
	T	338.7−373.2	98.9 ± 0.2	100.4 ± 0.2	this work
4-nitrophenol (l)				85.4[c,d]	this work
5-methyl-2-nitrophenol (cr)	T	288.3−326.2	81.1 ± 0.3	81.4 ± 0.3	this work
5-methyl-2-nitrophenol (l)	T	331.2−358.2	59.3 ± 0.5	62.8 ± 0.5	this work
2-methyl-5-nitrophenol (cr)	T	333.4−374.3	101.1 ± 0.3	102.7 ± 0.3	this work
2-methyl-5-nitrophenol (l)				85.9[c,d]	this work
3-methyl-4-nitrophenol (cr)	T	333.2−376.4	106.6 ± 0.4	108.3 ± 0.4	this work
3-methyl-4-nitrophenol (l)				85.8[c,d]	this work

[a] Techniques: E = ebulliometry; C = calorimetry; TE = torsion and mass-loss effusion technique; K = Knudsen mass-loss effusion technique; T = transpiration. [b] Original vapor pressures available in the literature were treated using eqs 2 and 3 in order to evaluate the enthalpy of sublimation at 298.15 K in the same way as our own results in Table 4. [c] Enthalpy of vaporization $\Delta^g_l H_m$. [d] Calculated as the difference $\Delta^g_l H_m = \Delta^g_{cr} H_m - \Delta^l_{cr} H_m$; values of fusion enthalpies, $\Delta^l_{cr} H_m$, are collected in the Table 5.

deriving enthalpies of sublimation. Having established new reliable data for thermochemical properties of nitrophenols, we need to prove its consistency. One of the best ways to do this is to perform thermochemical investigations of a series of parent compounds such as nitrocresols (see Figure 1), where the dominating interactions of the substituents (OH and NO_2) on the benzene ring are essentially the same as in the nitrophenols; however, additional interactions of OH and NO_2 with the CH_3 group have to be taken into account. Provided that both data sets for nitrophenols and nitrocresols are internally consistent, it should be possible to ensure that the uncertainty in the available thermochemical data on nitrophenols can be resolved. Hence, in addition to the remeasurements on 2-, 3-, and 4-nitrophenols, the three nitrocresols (see Figure 1) have also been studied.

Enthalpies of Formation ($\Delta_f H^\circ_m$(cr)) of Nitrophenols and Nitrocresols. The results of typical combustion experiments for nitrophenols are summarized in Table 3. The means of individual values of the standard massic energies of combustion $\Delta_c u^\circ$, were derived as a rule from 6 to 10 independent experiments. To derive $\Delta_f H^\circ_m$(cr) from the molar enthalpy of combustion $\Delta_c H^\circ_m$, molar enthalpies of formation of $H_2O(l) = -285.830 \pm 0.042$ kJ·mol^{-1} and $CO_2(g) = -393.51 \pm 0.13$ kJ·mol^{-1} have been used as assigned by *CODATA*.[17] Table 1 lists the derived standard molar enthalpies of combustion and the standard molar enthalpies of formation of the nitrophenols and nitrocresols derived in this work and provides comparison with the available results. The total uncertainty was calculated according to the guidelines presented by Olofsson.[25] The uncertainty assigned to $\Delta_f H^\circ_m$ is twice the overall standard

TABLE 3: Results for Typical Combustion Experiments with Nitrophenols and Nitrocresols at 298.15 K[a]

	2-Nitrophenol	3-Nitrophenol	4-Nitrophenol
m(substance)/g[b]	0.68433	0.77231	0.76271
m'(cotton)/g[b]	0.00382	0.00436	0.00331
ΔT_c/K[c]	1.03363	1.05038	1.03359
$(\epsilon_{calor})(-\Delta T_c)$/J	−15984.22	−16066.89	−15810.06
ΔU_{corr}/J[d]	11.1	13.1	12.9
$-m'\Delta_c u'$/J	64.89	73.88	56.09
$\Delta_c u^0$(substance)/J g^{-1}	−20668.1	−20597.7	−20581.7

	5-Methyl-2-nitrophenol	2-Methyl-5-nitrophenol	3-Methyl-4-nitrophenol
m(substance)/g[b]	0.74234	0.74467	0.69433
m'(cotton)/g[b]	0.00382	0.00296	0.00383
ΔT_c/K[c]	1.11900	1.12082	1.04563
$(\epsilon_{calor})(-\Delta T_c)$/J	17116.51	17144.35	−15994.23
ΔU_{corr}/J [d]	12.2	12.3	11.4
$-m'\Delta_c u'$/J	64.73	50.16	64.90
$\Delta_c u^0$(substance)/J g^{-1}	−22899.3	−22882.8	−22869.9

[a] For the definition of the symbols, see ref 14. T_h = 298.15 K; V(bomb) = 0.3200 dm^3; p^i(gas) = 3.04 MPa; m^i(H$_2$O) = 1.00 g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\epsilon_{cont})(-\Delta T_c) = (\epsilon^i_{cont})(T^i - 298.15\text{ K}) + (\epsilon^f_{cont})(298.15\text{ K} - T^f + \Delta T_{corr})$. [d] ΔU_{corr}, the correction to the standard state, is the sum of items 81−85, 87−90, 93, and 94 in ref 14.

deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

Previous experimental values of $\Delta_f H°_m$(cr) of 3-nitrophenol have been determined by Ribeiro da Silva et al.[12] using static-bomb combustion calorimetry and by Sabbah and Gouali[13] using microbomb combustion calorimetry. Their values are in disagreement by 5 kJ·mol^{-1}, but our new value of −209.3 ± 1.3 kJ·mol^{-1} is in acceptable agreement with the result obtained by Ribeiro da Silva et al.[12] Previous determinations of $\Delta_f H°_m$(cr) of 4-nitrophenol using static-bomb combustion calorimetry[11] and microbomb combustion calorimetry[13] are also in disagreement by 5 kJ·mol.$^{-1}$ Our new value of −214.5 ± 1.2 kJ·mol^{-1} is in agreement with the value obtained by Finch et al.[11] within the boundaries of the experimental uncertainties (see Table 1).

Vapor-Pressure Measurements on Nitrophenols and Nitrocresols. Vapor pressures of nitrophenols and nitrocresols obtained by the transpiration method were fitted using the following equation[15]

$$R \ln p_i^{sat} = a + \frac{b}{T} + \Delta_{cr}^{g} C_p \ln\left(\frac{T}{T_0}\right) \tag{2}$$

where a and b are adjustable parameters. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature, which has been chosen to be 298.15 K. Consequently, the expression for the sublimation enthalpy at temperature T is derived

$$\Delta_{cr}^{g} H_m(T) = -b + \Delta_{cr}^{g} C_p T \tag{3}$$

Experimental results with parameters a and b are listed in Table 4. Values of $\Delta_{cr}^{g} C_p$ have been derived according to a procedure developed by Chickos and Acree.[26] When the vapor pressures of liquid samples of nitrophenol or nitrocresol derivatives were measured, eq 2 gives the expression for the vaporization enthalpy $\Delta_l^g H_m$ at temperature T. Values of $\Delta_l^g C_p$ required for the data treatment in this case have been derived according to a procedure developed by Chickos and Acree.[26] We have checked our procedure by using measurements of vapor pressures of n-alcohols[15] and substituted naphthalenes.[27] It turned out that vapor pressures derived from the transpiration method were reliable within 1−3%. Experimental results and parameters a and b according to eq 2 are listed in Tables 2 and 4.

Enthalpies of Sublimation of Nitrophenols and Nitrocresols. The set of available sublimation enthalpies, $\Delta_{cr}^{g} H_m$, of 2-nitrophenol shows a large spread of 30 kJ·mol^{-1} (see Table 2). The most recent calorimetric result published by Sabbah et al.[13] is 3.1 kJ·mol^{-1} lower than our value. For other less volatile isomers, the difference becomes even more profound, 6.5 kJ·mol^{-1} for 3-nitrophenol and 8.5 kJ·mol^{-1} for 4-nitrophenol (see Table 2), and we do not have any explanation for this fact. However, it should be mentioned that disagreements of available results with those reported by Sabbah et al.[13] have been often found in the literature.[33,34]

Available experimental data on the vapor pressures of 3-nitrophenol (see Table 2) are also in disarray. However, the most recent vapor pressures measured by Ribeiro da Silva et al.[12] using the Knudsen technique are generally close to our results (see Figure 2), and only a few experimental points from ref 12 at lower temperatures are in disagreement with ours, resulting in a difference of the sublimation enthalpies of about 2 kJ·mol^{-1}. For 4-nitrophenol, the sublimation enthalpies derived in this work are in very close agreement with those from the Knudsen technique.[32]

Enthalpies of Vaporization of Nitrophenols and Nitrocresols. Since significant discrepancies in the experimental results collected for sublimation enthalpies in the Table 2 have been found, additional arguments to support the reliability of our new measurements are required. A valuable test of the consistency of the experimental data on the vaporization and sublimation enthalpies measured in this work is the comparison of the enthalpy of fusion, $\Delta_{cr}^{l} H_m$, of 2-nitrophenol obtained by direct measurements (differential scanning calorimetry, DSC) with the difference of experimental values according to the equation

$$\Delta_{cr}^{l} H_m = \Delta_{cr}^{g} H_m - \Delta_{l}^{g} H_m \tag{4}$$

To do this, 2-nitrophenol was investigated by the transpiration method above and below the melting point, and values for $\Delta_{cr}^{g} H_m$ (298.15 K) and $\Delta_{l}^{g} H_m$ (298.15 K) were derived. According to eq 4, we obtained $\Delta_{cr}^{l} H_m$ (298.15 K) = (17.0 ± 0.6) kJ·mol^{-1}. Independent experimental enthalpies of the fusion of 2-nitrophenol measured by DSC[13,35,36] at the melting temperature

TABLE 4: Experimental Results of the Vapor Pressure *p* of Nitrophenols and Nitrocresols Using the Transpiration Method

T/K[a]	m/mg[b]	$V(N_2)$/dm^3 [c]	N_2-flow/dm^3·h^{-1}	p/Pa[d]	$(p_{exp} - p_{calc})$/Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$/kJ·mol^{-1}
2-nitrophenol (l); $\Delta_{cr}^{g}H_m$ (298.15 K) = 75.37 ± 0.39 kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{300.6}{R} - \frac{83037.0}{R(T/\text{K})} - \frac{25.7}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
281.3	7.42	58.93	2.52	2.24	−0.04	75.81
285.3	11.16	53.93	2.53	3.67	0.08	75.71
289.3	13.43	41.32	2.53	5.76	0.18	75.60
292.3	3.41	7.93	2.53	7.61	−0.10	75.53
295.3	2.96	5.10	2.53	10.29	−0.29	75.45
298.3	3.32	4.13	2.53	14.21	−0.19	75.37
301.2	2.91	2.70	2.53	19.07	−0.23	75.30
304.4	3.26	2.23	2.53	25.80	−0.67	75.22
307.3	3.02	1.55	2.52	34.41	−0.62	75.14
310.4	8.81	3.23	2.52	48.18	1.19	75.06
311.3	3.08	1.05	2.53	51.71	0.60	75.04
313.2	2.64	0.759	2.53	61.51	0.57	74.99
316.2	2.49	0.557	2.53	79.19	−0.89	74.91
2-nitrophenol (l); $\Delta_{l}^{g}H_m$ (298.15 K) = 58.40 ± 0.50 kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{291.9}{R} - \frac{79361.4}{R(T/\text{K})} - \frac{70.3}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
319.2	4.35	0.761	2.54	101.28	−0.67	56.93
322.1	4.67	0.676	2.54	122.41	−1.22	56.72
325.2	5.26	0.613	2.54	152.08	0.84	56.50
328.2	5.44	0.528	2.54	182.32	−0.70	56.29
331.2	5.35	0.423	2.54	224.16	3.60	56.08
334.2	5.06	0.338	2.54	264.73	0.01	55.87
337.2	4.94	0.275	2.54	318.20	1.71	55.66
340.3	4.50	0.211	2.54	376.59	−2.52	55.44
343.2	4.35	0.169	2.54	455.28	8.02	55.24
346.2	3.70	0.127	2.54	516.49	−12.31	55.03
3-nitrophenol (cr,II); $\Delta_{cr}^{g}H_m$ (298.15 K) = (97.51 ± 0.32) kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{320.3}{R} - \frac{105170.9}{R(T/\text{K})} - \frac{25.7}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
323.2	1.79	76.07	3.15	0.42	0.00	96.87
326.2	2.51	76.14	3.15	0.58	0.00	96.79
329.3	1.97	42.93	3.15	0.81	0.00	96.71
332.1	2.88	45.68	3.15	1.11	0.01	96.64
333.2	2.88	41.31	3.06	1.23	−0.01	96.61
335.1	5.82	67.95	3.15	1.51	0.01	96.56
336.5	3.22	33.26	3.08	1.71	−0.03	96.52
338.1	3.12	27.15	3.15	2.03	−0.02	96.48
341.3	3.38	20.99	3.06	2.84	0.02	96.40
343.2	2.49	13.00	3.08	3.39	−0.02	96.35
344.2	0.29	1.36	3.08	3.78	0.02	96.33
347.3	2.33	8.25	3.08	5.00	−0.08	96.25
350.3	3.44	8.78	3.08	6.92	0.16	96.17
353.3	3.08	6.07	3.08	8.96	0.02	96.09
355.2	2.45	4.16	3.08	10.44	−0.22	96.04
3-nitrophenol (cr,I); $\Delta_{cr}^{g}H_m$ (298.15 K) = 97.83 ± 1.3 kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{320.8}{R} - \frac{105488.9}{R(T/\text{K})} - \frac{25.7}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
357.2	2.45	3.60	3.08	12.05	−0.15	96.31
359.2	2.37	2.90	3.08	14.48	−0.13	96.26
361.3	2.15	2.16	3.08	17.67	0.05	96.20
363.3	2.17	1.82	3.08	21.10	0.08	96.15
365.3	2.01	1.41	3.08	25.23	0.21	96.10
367.3	2.82	1.72	3.08	28.95	−0.78	96.05
369.3	2.29	1.15	3.08	35.13	−0.12	96.00

TABLE 4: Continued

T/K[a]	m/mg[b]	$V(N_2)$/dm^3 [c]	N_2-flow/dm^3·h^{-1}	p/Pa[d]	$(p_{exp} - p_{calc})$/Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$/kJ·mol^{-1}
4-nitrophenol (cr); $\Delta_{cr}^{g}H_m$ (298.15 K) = 100.39 ± 0.21 kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{318.3}{R} - \frac{108054.3}{R(T/\text{K})} - \frac{25.7}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
338.7	1.63	46.55	3.70	0.62	0.003	99.35
343.7	3.48	59.76	3.60	1.03	0.002	99.22
346.1	2.99	41.22	3.60	1.28	−0.023	99.16
349.2	3.01	29.92	3.74	1.78	0.008	99.08
352.0	3.32	25.43	3.74	2.30	−0.022	99.01
355.3	3.80	21.21	3.74	3.17	−0.016	98.92
358.6	3.52	14.58	3.60	4.27	−0.061	98.84
361.7	3.57	11.09	3.60	5.69	−0.066	98.76
364.5	3.99	9.54	3.60	7.39	−0.022	98.69
367.0	2.72	5.17	3.74	9.31	0.058	98.62
369.2	2.78	4.39	3.74	11.19	−0.027	98.57
371.3	2.67	3.49	3.74	13.51	0.057	98.51
373.2	2.38	2.68	3.74	15.70	−0.119	98.46
5-methyl-2-nitrophenyl (cr); $\Delta_{cr}^{g}H_m$ (298.15 K) = 81.36 ± 0.25 kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{311.9}{R} - \frac{90274.1}{R(T/\text{K})} - \frac{29.9}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
288.3	2.47	41.77	3.36	0.95	−0.02	81.66
293.2	3.48	32.93	3.36	1.70	−0.01	81.51
298.2	4.00	21.50	3.36	2.99	0.00	81.36
303.4	2.29	6.97	3.36	5.28	0.03	81.20
307.4	1.50	2.97	3.36	8.10	0.11	81.08
310.3	3.22	4.93	3.36	10.49	−0.25	81.00
313.3	3.11	3.42	3.36	14.64	0.13	80.91
316.3	2.93	2.44	3.36	19.35	−0.12	80.82
319.2	3.58	2.27	3.36	25.38	−0.36	80.73
322.2	2.85	1.34	3.36	34.10	−0.07	80.64
324.3	3.14	1.23	3.36	40.94	−0.58	80.58
326.2	2.57	0.840	3.36	49.22	−0.20	80.52
5-methyl-2-nitrophenol (cr); $\Delta_{l}^{g}H_m$ (298.15 K) = 62.84 ± 0.50 kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{303.0}{R} - \frac{85978.3}{R(T/\text{K})} - \frac{77.6}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
331.2	5.96	1.40	3.36	68.40	−0.72	60.28
334.2	6.85	1.32	3.36	83.59	−0.50	60.05
337.2	7.03	1.12	3.36	100.8	−1.1	59.82
340.3	6.90	0.896	3.36	123.7	−0.1	59.57
343.3	6.77	0.728	3.36	149.4	0.7	59.34
346.3	7.66	0.700	3.36	175.7	−2.2	59.11
349.3	7.47	0.560	3.36	214.4	2.2	58.88
352.3	7.08	0.448	3.36	253.9	1.8	58.64
355.2	7.06	0.392	3.36	289.1	−7.6	58.42
358.2	9.09	0.420	3.36	347.7	−2.4	58.19
2-methyl-5-nitrophenol (l); $\Delta_{cr}^{g}H_m$ (298.15 K) = 102.73 ± 0.33 kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{331.4}{R} - \frac{111647.6}{R(T/\text{K})} - \frac{29.9}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
333.4	1.15	42.07	3.03	0.44	0.00	101.68
338.4	2.04	44.29	3.03	0.74	−0.01	101.53
345.4	1.53	15.45	3.03	1.59	0.03	101.32
350.3	1.83	11.54	3.03	2.55	−0.01	101.18
353.3	2.55	11.77	3.03	3.49	0.05	101.09
356.3	1.88	6.51	3.03	4.65	0.05	101.00
358.2	2.61	7.50	3.03	5.58	0.08	100.94
361.3	2.71	5.91	3.03	7.37	0.01	100.85
364.3	2.75	4.57	3.03	9.66	−0.05	100.76
367.3	2.32	2.93	3.03	12.75	0.01	100.67
371.3	2.36	2.07	3.03	18.31	0.14	100.55
374.3	2.45	1.69	3.03	23.24	−0.34	100.46

TABLE 4: Continued

T/K[a]	m/mg[b]	V(N_2)/dm^3 [c]	N_2-flow/dm^3·h^{-1}	p/Pa[d]	($p_{exp} - p_{calc}$)/Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$/kJ·mol^{-1}
3-methyl-4-nitrophenol (cr); $\Delta_{cr}^{g}H_m$ (298.15 K) = 108.31 ± 0.36 kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{338.3}{R} - \frac{117221.0}{R(T/\mathrm{K})} - \frac{29.9}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$						
333.2	1.23	149.8	3.38	0.13	0.00	107.26
338.2	1.53	104.8	3.42	0.23	0.00	107.11
344.5	1.35	47.48	3.42	0.46	−0.01	106.92
348.2	1.92	45.80	3.42	0.67	−0.02	106.81
353.3	1.00	13.58	3.42	1.18	−0.01	106.66
358.3	1.23	10.10	3.42	1.96	0.00	106.51
361.4	1.79	10.50	3.42	2.73	0.06	106.42
364.4	2.04	9.19	3.42	3.57	0.00	106.33
367.4	1.92	6.68	3.42	4.63	−0.13	106.24
370.4	2.02	5.14	3.42	6.32	0.02	106.15
373.4	2.16	4.17	3.42	8.33	0.02	106.06
376.4	2.30	3.42	3.42	10.78	−0.13	105.97

[a] Temperature of saturation. N_2 gas flow 2 to 3.5 dm^3·h^{-1}. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer the mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at T = 243 K.

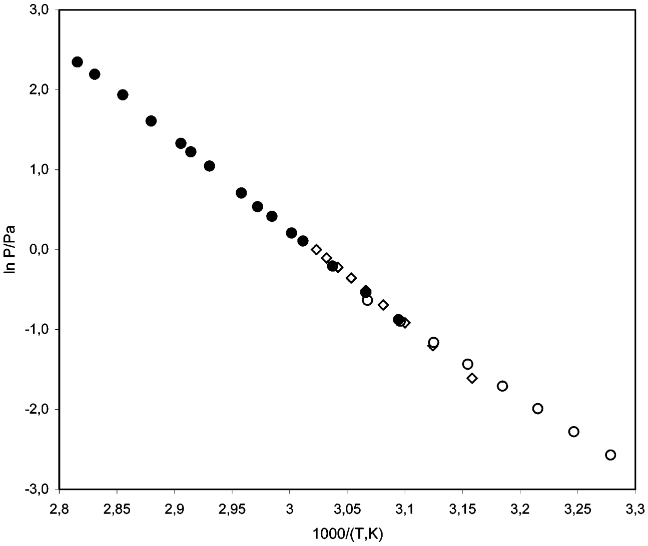


Figure 2. Plot of vapor pressure against reciprocal temperature for the liquid 3-nitrophenol. Key: ○, ref 30; ◇, ref 12; ●, this work.

TABLE 5: Compilation of Experimental Data on Enthalpies of Fusion, $\Delta_{cr}^{l}H_m$, of Nitrophenols and Nitrocresols

compound	$\Delta_{cr}^{l}H_m$at T_{fus} (kJ·mol^{-1})	T_{fus} (K)	$\Delta_{cr}^{l}H_m$at 298 K (kJ·mol^{-1})	ref
2-nitrophenol	17.45	318.0	16.6	35
	18.32	318.4	17.4	13
	17.91	318.6	17.0	36
			17.0 ± 0.6	average
3-nitrophenol	19.20	370.0	16.0	35
	21.30	370.0	18.1	37
	20.54	370.5	17.3	13
	21.35		18.2	38
	19.96	370.0	16.9	42
			17.3 ± 0.8	average
4-nitrophenol	18.25	370.0	15.3	35
	19.30	368.8	16.2	37
	17.33	387.3	13.4	13
	18.86	386.1	14.9	36
			15.0 ± 1.2	average
5-methyl-2-nitrophenol	20.8	327.8	19.4	39,40
2-methyl-5-nitrophenol		386.0	16.8[a]	
3-methyl-4-nitrophenol	27.41	401.0	22.5	39,40

[a] Calculated using the modified[41] Walden's rule: $\Delta_{cr}^{l}H_m$ (T_{fus}) = 54.4 (J·K^{-1} mol^{-1})T_{fus} (K).

T_{fus} are listed in Table 5. Because of the deviation of the reference temperature T = 298.15 K from the T_{fus} in Table 5, the experimental enthalpy of fusion of 2-nitrophenol had to be adjusted to the reference temperature. The adjustment was calculated from the equation[26]

$$\{\Delta_{cr}^{l}H_m(T_{fus}/\mathrm{K}) - \Delta_{cr}^{l}H_m(298.15\ \mathrm{K})\}/(\mathrm{J{\cdot}mol^{-1}}) = \{(0.75 + 0.15\ C_p^{cr})[(T_{fus}/\mathrm{K}) - 298.15]\} - \{(10.58 + 0.26\ C_p^{l})[(T_{fus}/\mathrm{K}) - 298.15]\} \quad (5)$$

where the value of $\Delta_{cr}^{l}C_p$ has been derived from the experimental isobaric molar heat capacity of liquid 2-nitrophenol, C_p^{l}, and the isobaric molar heat capacities of the solid 4-nitrophenol, C_p^{cr}, calculated according to the procedure given in ref 26. With this adjustment (the uncertainty of the correlation was not taken into account), the standard enthalpy of fusion at T = 298.15 K, $\Delta_{cr}^{l}H_m$ (298.15 K) = 17.0 ± 0.6 kJ·mol^{-1} was calculated from the average value of the data available in the Table 5. Thus, $\Delta_{cr}^{l}H_m$ calculated from the difference $\Delta_{cr}^{g}H_m$ − $\Delta_{l}^{g}H_m$ measured in this work is identical with $\Delta_{cr}^{l}H_m$ measured by calorimetry and adjusted to T = 298.15 K.

In the same way, 5-methyl-2-nitrophenol was investigated by the transpiration method above and below the melting point, and values for $\Delta_{cr}^{g}H_m$ (298.15 K) and $\Delta_{l}^{g}H_m$ (298.15 K) were derived. Using eq 4, we obtained $\Delta_{cr}^{l}H_m$ (298.15 K) = 18.6 ± 0.6 kJ·mol^{-1}. The enthalpy of fusion $\Delta_{cr}^{l}H_m$ (298.15 K) = 19.4 kJ·mol^{-1} was calculated from direct calorimetric data in Table 5, being in close agreement with the enthalpy of fusion $\Delta_{cr}^{l}H_m$ calculated from the difference $\Delta_{cr}^{g}H_m$ − $\Delta_{l}^{g}H_m$ measured in this work. Thus, our results for vaporization and sublimation enthalpies of 2-nitrophenol and 5-methyl-2-nitrophenol have been proved to be consistent.

3-Nitrophenol is a solid at room temperature with the (cr,II) crystal structure.[42] At 356 K, 3-nitrophenol transforms into a crystal phase (cr,I) which melts at 370 K.[42] In this work, we have performed extended vapor-pressure measurements of 3-nitrophenol for both cr,I and cr,II modifications, and its appropriate enthalpies of sublimation have been obtained (see

TABLE 6: Results of Predicted Standard Enthalpy of Formation $\Delta_f H^\circ_m$(g) (in kJ·mol^{-1}) for Nitrophenols and Nitrocresols in the Gaseous Phase at 298.15 K[a]

	MP2/ 6-3G(d,p)	MP2/ 6-311G++(d,p)	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311+G(d,p)	G2MP2	G3MP2	exp
2-nitrophenol	−127.0	−119.8	−136.1	−130.3	−124.6	−124.2	−127.8 ± 1.2
3-nitrophenol	−115.3	−112.8	−111.6	−111.0	−110.7	−110.8	−111.8 ± 1.3
4-nitrophenol	−114.2	−111.8	−117.2	−117.0	−114.0	−114.5	−114.1 ± 1.2
5-methyl-2-nitrophenol	−157.2	−160.2	−170.2	−165.2	−160.6	−160.4	−167.6 ± 1.3
2-methyl-5-nitrophenol	−144.7	−152.9	−141.1	−141.4	−148.3	−148.9	−147.2 ± 1.1
3-methyl-4-nitrophenol	−134.0	141.0	−138.0	−136.2	−138.3	−140.7	−144.9 ± 1.3

[a] Reaction II for nitrophenols or reaction III for methylnitrophenols.

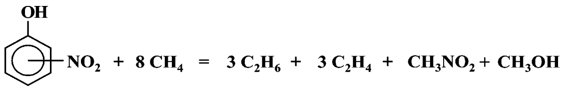
Tables 2 and 4). Additional evidence of the consistency of our experimental data on the sublimation enthalpies of 3-nitrophenol (see Table 4) is provided by comparing the difference $\Delta^g_{cr}H_m$(cr, II) − $\Delta^g_{cr}H_m$(cr, I) = {(97.8−97.5) = 0.3} kJ·mol^{-1} (referred to 298.15 K) with the experimental enthalpy of phase transition, ΔH_{trs}(356 K) = 0.2 kJ·mol^{-1}, measured by DSC.[42] Thus, the enthalpy of the phase transition calculated from the difference of $\Delta^g_{cr}H_m$ of the two crystalline phases measured in this work is indistinguishable from the value measured directly by calorimetry.

The comparison of the enthalpies of vaporization of the ortho, meta, and para isomers of nitrophenol shows that the $\Delta^g_l H_m$ values of ortho-nitro-substituted species are about 25 kJ·mol^{-1} lower (see Table 2) than those of meta and para isomers. Such a decrease is typical for substituted benzenes.[34] It is also obvious from Table 2 that the vaporization enthalpies of meta- and para-substituted species (2-methyl-5-nitrophenol and 3-methyl-4-nitrophenol) are indistinguishable from one another within the boundaries of their experimental uncertainties. Such behavior is typical for the most of meta- and para-substituted benzenes.[43] Vaporization enthalpies of meta- and para-substituted species (3-nitrophenol and 4-nitrophenol) differ by ca. 5 kJ·mol^{-1} (see Table 2). This is quite understandable due to the higher symmetry of the 4-nitrophenol molecules, which causes a more structured liquid phase. As a consequence, somewhat more energy is required to transfer molecules in the gaseous phase in comparison with the less symmetrical 3-nitrophenol. The introduction of the methyl substituent into the benzene ring (2-methyl-5-nitrophenol and 3-methyl-4-nitrophenol) completely cancels the effect of symmetry on the packing of molecules in the liquid phase. As a result, the vaporization enthalpies of 2-methyl-5-nitrophenol and 3-methyl-4-nitrophenol become indistinguishable. Thus, the values of vaporization enthalpies and enthalpies of sublimation of nitrophenols derived in this work show internal consistency, and they can be used with high reliability for further calculation of the standard enthalpies of formation, $\Delta_f H^\circ_m$(g) at 298.15 K, of the nitrophenols (see Table 1).

Quantum Chemical Calculations for Nitrophenols and Nitrocresols. It has been shown recently that ab initio calculations are suitable to predict the formation enthalpies of substituted benzenes.[34,43] For this reason, experimental results of enthalpies of formation of all six compounds studied in the gaseous phase, $\Delta_f H^\circ_m$(g), have been compared with high-level ab initio calculations.

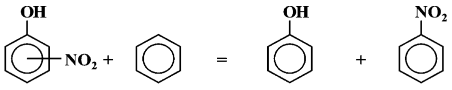
In standard Gaussian theories, theoretical enthalpies of formation are calculated through atomization reactions.[44] The agreement between theory and experiment can be improved when the calculation of the enthalpy of formation is based on a suitable isodesmic reaction rather than the atomization reaction.[44] In an isodesmic reaction, the number of bonds of each type is conserved on both sides of the chemical reaction equation, and therefore, a cancellation of errors can be expected (such errors might arise from the insufficient treatment of electron correlation and incompleteness of the basis sets). Further improvement in the calculation of the enthalpies of formation should be provided by so-called homodesmic reactions, where in addition to the types of bonds, the hybridization of the atoms in the bond is also conserved.

One of the disadvantages of the isodesmic and homodesmic reaction approach is that the calculated $\Delta_f H^\circ_m$(g) value crucially depends on the accuracy of the experimental enthalpies of formation taken as reference as well as on the choice of these reactions. In this work, we calculated the enthalpies of formation of nitrophenols with the help of an atomization procedure as well as both the isodesmic (type I) and the homodesmic (type II and III) reactions. The isodesmic scheme is based on the "bond separation reactions" of nitrophenol with methane where simple molecules are formed

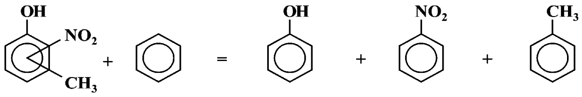


(I)

The homodesmic scheme is based on the distribution reaction of nitrophenol with benzene



(II)



(III)

By using the enthalpies of reactions I−III, calculated by MP, DFT, and G3 methods together with the enthalpies of formation, $\Delta_f H^\circ_m$(g), for benzene, toluene, nitrobenzene, phenol, methanol, nitromethane, methane, ethane, and ethene recommended by Pedley et al.,[45] the enthalpies of formation of nitrophenols have been calculated (see Tables 6 and 7). While the enthalpies of formation of nitrophenols calculated by MP and DFT methods using the isodesmic reactions II and III are in moderate but still acceptable agreement with the experimental data derived in this work (see Table 6), the enthalpies of formation of nitrophenols predicted by using the atomization procedure and the isodesmic reactions I−III are in excellent agreement with the experimental data. Since the method of G3(MP2) is the most sophisticated one, enthalpies of formation calculated by G3(MP2) have been averaged (atomization and isodesmic reactions) and are given in Table 1 fordirect comparison with the experimental data.

Nitrophenols have attracted much attention from computational chemistry; e.g., Chen et al.[46] has reported averaged $\Delta_f H^\circ_m$(g) values calculated by using nine different DFT methods with help of the isodesmic reaction

$$C_6H_5NO_3 + NH_3 = C_6H_5OH + NH_2NO_2$$

TABLE 7: Results of Calculation of the Standard Enthalpy of Formation $\Delta_f H^\circ_m$(g) (in kJ·mol^{-1}) for Nitrophenols and Nitrocresols in the Gaseous Phase at 298.15 K[a]

	G2MP2		G3MP2		
	atomization	reaction I	atomization	reaction I	exp
2-nitrophenol	−133.3	−128.6	−126.7	−126.0	−127.8 ± 1.2
3-nitrophenol	−119.4	−114.8	−113.3	−112.6	−111.8 ± 1.3
4-nitrophenol	−122.7	−118.1	−117.0	−116.2	−114.1 ± 1.2
5-methyl-2-nitrophenol	−169.3	−166.5	−163.5	−162.7	−167.6 ± 1.3
2-methyl-5-nitrophenol	−157.0	−154.2	−152.1	−151.2	−147.2 ± 1.1
3-methyl-4-nitrophenol	−147.6	−144.8	−143.8	−143.0	−144.9 ± 1.3

[a] Atomization procedure and reaction I.

Their results for 2-, 3-, and 4-nitrophenol are as follows: −124.7, −103.2, and −108.7 kJ·mol^{-1}, and they are in disagreement (except for 2-nitrophenol) by (5 to 8) kJ·mol^{-1} with the experimental results reported in this work.

Analysis of Substituent Effects in Nitrophenols and Nitrocresols. The energetics of the mutual interactions of substituents in nitrophenols should reflect the expected strong resonance stabilization by π-electron donation from phenolic hydroxyl group to the strongly π-electron-withdrawing nitro group with additional stabilization of the ortho isomer by intramolecular hydrogen bonding. How can this energetics be assessed quantitatively? The total energetics of substituent effects can be examined in different ways. Group additivity procedures are conventionally applied to derive substituent effects (or strain enthalpies) as the differences between the observed enthalpies of formation in the gaseous state and values calculated by applying any of the different group-additivity schemes.[47,48] On this basis, we have discussed the substituent effects of benzene derivatives recently.[49,50] In this work, a quantitative analysis of substituent effects has been made by adjusting a common group-additivity procedure to the phenol derivatives with parameters that include two types of contributions: (a) increments for the substitution of H atoms by NO$_2$, OH, or CH$_3$ substituents in the standard series starting with benzene, or (b) pairwise interactions of NO$_2$, OH, and CH$_3$ with respect to their positions in the benzene ring (ortho, meta, and para).

Parameters of the type *b* provide a quantitative insight into the energetics of mutual interactions of substituents in the benzene ring.

The formula used for calculating the formation enthalpy of 2-nitrophenol is

$$\Delta_f H^\circ_m(\mathrm{g})(\text{2-nitrophenol}) = \Delta_f H^\circ_m(\mathrm{B}) + \Delta H(\mathrm{H} \rightarrow \mathrm{OH}) + \Delta H(\mathrm{H} \rightarrow \mathrm{NO_2}) + (\text{ortho OH}-\mathrm{NO_2})$$

where $\Delta_f H^\circ_m$(B) is the enthalpy of formation of benzene; ΔH(H → OH) is an increment of the H → OH substitutions on the benzene ring; ΔH(H → NO$_2$) is an increment of the H → NO$_2$ substitutions on the benzene ring; and (ortho OH−NO$_2$) is the mutual interaction of OH and NO$_2$.

The corresponding formula for 5-methyl-2-nitrophenol is somewhat more complex

$$\Delta_f H^\circ_m(\text{5-methyl-2-nitrophenol}) = \Delta_f H^\circ_m(\mathrm{B}) + \Delta H(\mathrm{H} \rightarrow \mathrm{OH}) + \Delta H(\mathrm{H} \rightarrow \mathrm{NO_2}) + \Delta H(\mathrm{H} \rightarrow \mathrm{CH_3}) + (\text{ortho OH}-\mathrm{NO_2}) + (\text{meta OH}-\mathrm{CH_3}) + (\text{para NO}_2-\mathrm{CH_3})$$

where ΔH(H → CH$_3$) is an additional increment of H → CH$_3$ substitutions on the benzene ring. The pairwise interactions of the introduced CH$_3$ group with other groups were taken into account through the corresponding additional corrections (meta OH−CH$_3$) and (para NO$_2$−CH$_3$).

TABLE 8: Parameters for the Calculation of the Gaseous Enthalpy of Formation, $\Delta_f H^\circ_m$(g) for Nitrophenols and Nitrocresols at T = 298.15 K (in kJ·mol^{-1})

group contribution	value/$\Delta_f H^\circ_m$(g)
C$_6$H$_6$	82.6 ± 0.7[45]
ΔH(H → NO$_2$)	−15.1 ± 1.0[45]
ΔH(H→OH)	−179.0 ± 1.1[45]
ΔH(H → CH$_3$)	−32.2 ± 0.9[45]
ortho OH−NO$_2$	−17.0 ± 0.9
meta OH−NO$_2$	−1.1 ±0.8
para OH−NO$_2$	−3.1 ± 0.9
(ortho OH−NO$_2$)$_{\mathrm{nonHB}}$	21.4
meta CH$_3$−OH	−1.5 ± 0.5[50]
ortho CH$_3$−NO$_2$	2.1 ± 0.5[49]
meta NO$_2$−NO$_2$[a]	11.0 ± 0.6
para CH$_3$−NO$_2$[a]	−4.7 ± 0.8

[a] From Table S1 (Supporting Information).

We have carried out a regression analysis of the experimental gaseous enthalpies of formation of nitrophenols (see Table 1) as a function of the number of substituents in the ring and their pairwise ortho, meta, and para interactions, respectively. The matrix of the parameters and experimental values involved in our calculations is presented in Table S1 (Supporting Information). The method of the polyfunctional least squares was used to evaluate the additive parameters, which are presented in the Table 8.

These parameters reveal that *o*-nitrophenols (2-nitrophenol and 5-methyl-2-nitrophenol) are distinctly stabilized in the gaseous phase by 16 kJ·mol^{-1} (see Table 8) due to intramolecular HB. Meta and para interactions of OH and NO$_2$ substituents slightly stabilize the molecule by about 2.5 kJ·mol^{-1}. Also, a weak stabilization of about 1−3 kJ·mol^{-1} is the result of the meta and para interactions of the OH and NO$_2$ substituents.

Strength of Intramolecular Hydrogen Bond in *o*-Nitrophenol. Several experimental techniques are available to demonstrate the presence of the intramolecular hydrogen bond in *o*-nitrophenol such as OH-stretching vibration-frequency shifts, OH-torsional vibration-frequency shifts, and hydroxyl-proton chemical shifts.[51] It is well-established that *o*-nitrophenol exists in the gaseous phase and in solution as mixtures of two conformers, a trans form with the hydroxyl hydrogen pointed away from the NO$_2$ group and a cis form with an intramolecular hydrogen bond. While spectroscopic data can provide qualitative

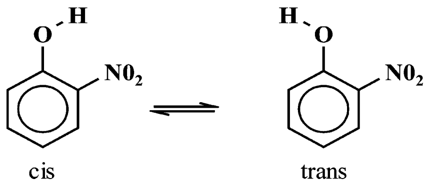


TABLE 9: Strength of the Intramolecular Hydrogen Bond $H_{\mathrm{H-bond}}$ (in kJ·mol^{-1}) in *o*-Nitrophenol

method of study	medium	$H_{\mathrm{H-bond}}$	ref
IR	CCl_4	25.9	5
IR	CCl_4	27.6	6
paper chromatograpy		25.5	55
gas chromatograpy	gas	35.0	7
B3LYP/6-31G(d,p)		49.8	20
B3LYP/6-31G(d,p)		44.8	8
B3LYP/6-31G**		47.9[a]	56
B3LYP/6-31G**		49.6[b]	56
MP2/6-3G(d,p)		38.4	this work
MP2/6-311G++(d,p)		26.1	this work
B3LYP/6-31G(d,p)		50.2	this work
B3LYP/6-311G++(3df,2p)		44.4	this work
G3MP2		33.4	this work
G3MP2		37.4[c]	this work
thermochemistry		38.4	this work

[a] Calculated from the OH rotation barrier (the barrier found in phenol was selected as the reference). [b] Calculated from NO_2 rotation barrier. [c] Calculated for 5-methyl-2-nitrophenol.

evidence of the intramolecular HB, it has been proven to be difficult to extract the energy of the interaction quantitatively. The strength of the hydrogen bond has been often discussed from the viewpoint of OH stretching frequency shifts and torsional-frequency shifts.[6] The enthalpy difference between the cis and trans forms of the ortho-substituted phenols could also be obtained by the method of temperature-dependent measurements of infrared intensities.[52] In this case, an equilibrium constant of the cis-to-trans isomerization of ortho-substituted phenol conformers has been measured directly at different temperatures. However, these measurements are difficult to apply to *o*-nitrophenol, because the equilibrium of the cis and trans forms of isomerization is shifted strongly to the cis form; therefore, no bands attributed to the trans conformer are observed up to 600 K in the vapor phase or in the solution. Compilation of the data of the strength of intramolecular HB for *o*-nitrophenol in the liquid phase available from the literature is given in Table 9. The level of 25 kJ mol^{-1} is typical for the HB strength in the liquid phase. This quantity in the liquid phase could be affected by the interactional influence of the solvent itself. At least such a suggestion is supported by the fact that the only experimental strength of the hydrogen bonding of 35 kJ mol^{-1} in *o*-nitrophenol available, the gaseous phase is noticeable large.[7] The question arises whether it is possible to verify this result by ab initio calculations. As a matter of fact, the definition of hydrogen-bond strength in an ab initio procedure is somewhat different from the experimental one. This energy is defined as the energetic difference of the H-bonded species (cis form) and the conformer with the hydroxyl group rotated by 180° around the C−O single bond (trans form) with subsequent geometry optimization. Our DFT calculations of HB strength for the gaseous phase expressed by the energy difference provide a substantial higher level of 45−50 kJ mol^{-1} (see Table 8). Fortunately, using the more sophisticated method of G3MP2 gives a value of 33.4 kJ mol^{-1}, in close agreement with that experimental value in the gaseous phase.[7] In addition, the enthalpy difference between the cis and trans forms of 5-methyl-2-nitrophenol as calculated by G3MP2 gives 37.4 kJ mol^{-1}, in acceptable agreement with that of 2-nitrophenol.

Thermochemistry is also able to contribute to the quantification of HB strength in *o*-nitrophenols. Indeed, in the case of *o*-nitrophenol, the energy of the pairwise interaction of the NO_2 and OH group is given as (ortho $OH-NO_2$) = −16.0 kJ·mol^{-1} (see Table 8). This value effectively consists of two contributions: the destabilizing effect from the steric ortho interaction of the neighboring groups, which are in close proximity, and the additional stabilizing effect, $H_{\mathrm{H-bond}}$, from the intramolecular hydrogen bonding between the NO_2 and OH group. The question arises how both of these effects in *o*-nitrophenol can be separated and how the hydrogen-bond strength $H_{\mathrm{H-bond}}$ can be extracted. For this purpose, we need to assess the destabilizing effect from the pure steric ortho interaction of the neighboring NO_2 and OH group using the gaseous enthalpy of formation for 2,6-dinitrophenol available in the literature[53]

$$\Delta_f H^\circ_m(\text{2,6-dinitrophenol}) = \Delta_f H^\circ_m(\mathrm{B}) + \Delta H(\mathrm{H} \rightarrow \mathrm{OH}) + 2\Delta H(\mathrm{H} \rightarrow \mathrm{NO_2}) + (\text{ortho } \mathrm{OH-NO_2}) + (\text{meta } \mathrm{NO_2-NO_2}) + (\text{ortho } \mathrm{OH-NO_2})_{\mathrm{nonHB}}$$

For this molecule, two nonequivalent ortho interactions (ortho $OH-NO_2$) and (ortho $OH-NO_2$)$_{\mathrm{nonHB}}$ could be ascribed. The first one has been defined above as the interaction with the specific intermolecular HB. Because the formation of the second HB in 2,6-dinitrophenol is not possible, the interaction (ortho $OH-NO_2$)$_{\mathrm{nonHB}}$ = 21.4 kJ·mol^{-1} should be responsible for the pure steric ortho interaction of the neighboring NO_2 and OH group, provided that the value of pairwise interaction (meta NO_2-NO_2) = 11.0 kJ·mol^{-1} is known from the enthalpy of formation of 1,3-dinitro-benzene.[54] Consequently, the simple difference of the two contributions

$$H_{\mathrm{H-bond}} = (\text{ortho } \mathrm{OH-NO_2}) - (\text{ortho } \mathrm{OH-NO_2})_{\mathrm{nonHB}} = (-17.0 - 21.4) = -38.4 \text{ kJ·mol}^{-1}$$

could be considered as a measure of the intramolecular hydrogen-bond strength. Although the separation of both effects is a very simplified point of view, such a procedure should provide additional quantitative information about the intramolecular hydrogen-bond strength in *o*-nitrophenol derived from thermochemical data on the gaseous enthalpies of formation. The resulting value of −38.4 kJ·mol^{-1} for hydrogen-bond strength in *o*-nitrophenol derived from thermochemistry is remarkably close to the result of 34.7 kJ·mol^{-1} derived for the gaseous phase experimentally[7] as well as the 33.4 kJ·mol^{-1} value obtained from high-level G3MP2 performed in this work (see Table 8).

Conclusions

The purpose of this work was to establish a consistent set of experimental thermochemical quantities for isomeric nitrophenols and nitrocresols. Our own results, together with a large number of experimental results from the literature, have been used to derive reliable values for the enthalpy of formation of the nitrophenols at the reference temperature 298.15 K. This collection together with the own results and high-level ab initio calculations helps to resolve previous contradictions in the experimental thermochemistry of nitrophenols with special emphasis on pairwise-substituent effects.

Supporting Information Available: Table S1, matrix of the parameters and experimental values involved in calculations of enthalpies of formation of nitrophenols for the analysis of substituent effects; Table S2, total energies at 0 K and enthalpies at 298.15 K (in hartree) of the molecules studied in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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